

PATENT SPECIFICATION

(11) 1390530

1390530

(21) Application No. 50487/72 (22) Filed 2 Nov. 1972

(44) Complete Specification published 16 April 1975

(51) INT CL² B01J 31/14 C07C 3/10

(52) Index at acceptance

B1E 302 360 36Y 421 422 42Y 462 463 491 49Y 549 552
55Y 578 579 580 584 61X 650 702 705 70Y 750 753
754 756 75X 75Y

C5E 7A1 7AY 8A8A1B 8A8A1C 8A8B1 8A8B2 8A8B3
8A8B4 8A8Y

(72) Inventors WOLFGAND SCHULZ, HERMANN MIX
ERHARD KURRAS,
FRIEDRICH-WILHELM WILCKE
JONATHAN REIHSIG, HANS FUHRMANN and
INGRID GRASSERT

(19)



(54) OLIGOMERISATION AND CO OLIGOMERISATION CATALYSTS

(71) We, AKADEMIE DER WISSENSCHAFTEN DER DDR OF RUDOWER CHAUSSE, Berlin, German Democratic Republic, a Corporation organised under the laws of the German Democratic Republic, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and 10 by the following statement:—

The present invention is concerned with a process for the production of heterogeneous catalysts suitable for the oligomerisation and co-oligomerisation of olefins, which catalysts have a good selectivity and a high activity.

It is known that olefins, especially propene, can be oligomerised with the help of solid catalysts which, as catalytically active components, contain cobalt or nickel or the oxides thereof. As carrier material, there are used various activated charcoals, aluminosilicates, optionally with the admixture of magnesium oxide, as well as aluminium oxides and zeolites. However, even when using comparatively high pressures and temperatures, the activity is scarcely satisfactory.

It is also known that aluminium oxide, silicon dioxide or aluminosilicate carriers which have been impregnated with a divalent nickel salt and a complex former or with monovalent nickel complexes and subsequently treated with an organo-aluminium compound or with an organo-metallic alkylating agent, can also be used to oligomerise olefins. Because of the low reactivity of these catalysts, it is necessary to use increased pressures and comparatively long reaction times.

Another group of known heterogeneous oligomerisation catalysts contain alkali metals as effective components. As carriers, there are used magnesium silicates, magnesium oxide, aluminium oxide, potassium carbonate,

activated charcoal or graphite, on to which are deposited the alkali metals or their hydrides or organo compounds, in finely-divided form. Since the activity of the catalysts thus obtained is low, they can also only be used at high pressures and reaction temperatures and with long residence times.

It is an object of the present invention to provide heterogeneous oligomerisation catalysts for olefins which do not suffer from the above-mentioned deficiencies and disadvantages and which show, under normal conditions, a high activity and good selectivity.

Thus, according to the present invention, there is provided a process for the production of heterogeneous oligomerisation and co-oligomerisation catalysts for olefins, wherein a completely hydrated aluminium oxide or a partially dehydrated aluminium hydroxide or hydroxide group-containing aluminium oxide carrier material is first thermally pre-treated, then reacted with at least one halogen-containing organo-aluminium compound and subsequently impregnated with at least one divalent nickel and/or divalent cobalt complex in which ligand atoms include oxygen, nitrogen, phosphorus, arsenic and/or antimony, the reaction and subsequent impregnation being carried out at a temperature of -50 to 150°C. and preferably of 0 to 60°C.

If desired, a divalent nickel and/or cobalt complex can be used in which one or two coordination positions of the central atom is occupied by an imino nitrogen atom.

As carrier materials, there can be used, for example, bayerite, hydrargillite, böhmite and γ-aluminium oxide.

For the reaction with the thermally pre-treated carrier materials, there can be used, for example, halogen-containing organo-

[Price 33p]

45

50

55

60

65

70

75

80

103 N.

aluminium compounds of the general formula



wherein X is a fluorine, chlorine, bromine or iodine atom and R is an alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, aralkyl or aralkenyl radical, triethyl aluminium sesquichloride or diethyl aluminium chloride being preferably used.

- 10 The reaction advantageously takes place in the temperature range of -50 to 100°C. and preferably at about 0°C., whereby, for 30 ml. of carrier material, there are used 20-50 ml. of halogen-containing organo-aluminium compound. The halogen-containing organo-aluminium compound can be applied to the carrier in diluted form or dissolved in an inert solvent. As solvent for the halogen-containing organo-aluminium compounds, there can be used, for example, not only aliphatic but also aromatic halogenated hydrocarbons, as well as pure aromatic, aliphatic or cycloaliphatic hydrocarbons.

- 25 The thermally pre-treated carrier materials reacted with the halogen-containing organo-aluminium compounds are loaded with divalent nickel and/or divalent cobalt complexes. As solvents, there can here also be used the above-mentioned hydrocarbons or halogenated hydrocarbons.

- 30 As divalent nickel complexes, there can be used, for example, bis-(salicylidene-iminato) nickel, bis-(N-n-butyl-salicylidene-iminato) nickel, bis-(N-n-dodecylsalicylidene-iminato) nickel, bis-(N-cyclohexyl-salicylidene-iminato) nickel, bis-(N-phenyl-salicylidene-iminato) nickel, bis-(N-o-chlorophenyl-salicylidene-iminato) nickel, bis-(N-o-pyridyl-salicylidene-iminato) nickel, bis-(2-amino-benzylidene-iminato) nickel, bis-[(N-n-butyl)-2-aminobenzylidene-iminato] nickel, bis-[(N-phenyl)-2-aminobenzylidene-iminato] nickel, bis-[(N-o-pyridyl)-2-aminobenzylidene-iminato] nickel, bis-[(N-n-butyl)-2-diphenyl-phosphine-benzylidene-iminato] nickel, bis-[(N-phenyl)-2-diphenylarsino-benzylidene-iminato] nickel, bis-(2-pyrrolidene-iminato) nickel, bis-[(o-chlorophenyl)-2-pyrrolidene-iminato] nickel, bis-(2-hydroxy-azobenzene) nickel, [(N-β-hydroxyethyl)-salicylidene-iminato] nickel, [(N-o-hydroxyphenyl)-salicylidene-iminato] nickel, [(N-β-methylaminoethyl)-2-pyrrolidene-iminato] nickel, 2,2'-dihydroxyazobenzene nickel, N,N'-bis-(salicylidene)-ethylenediamino nickel, N,N'-bis-(salicylidene)-o-phenylenediamino nickel, N,N'-bis-(2-pyrrolidene)-o-phenylenediamino nickel, N,N'-bis-(2-pyrrolidene)-

1,2-diphenyl-ethylenediamino nickel and nickel acetyl acetonate, as well as the complex formed between nickel acetyl acetonate and triphenyl phosphine.

In the same way, there can also be used the corresponding divalent cobalt complexes.

Furthermore, mixtures of divalent nickel and/or divalent cobalt complexes can be used.

The divalent nickel complexes can, in general, be prepared quickly and simply and are easy to purify. The *o*-substituted aryl-aldimine or aryl-ketimine nickel complexes, for example, the salicylaldimine, *o*-aminobenzaldimine, pyrrole-*α*-aldimine or *o*-hydroxyacetophenoneimine nickel complexes can be obtained by reacting a slight excess of primary amine in a polar solvent, such as ethanol or a halogenated aliphatic hydrocarbon, with the bis-*o*-hydroxy- or bis-*o*-aminobenzaldehyde or bis-*o*-hydroxy- or bis-*o*-aminoaryl ketone nickel complex. The metal ion can also be homogeneously reacted in aqueous or alcoholic solution with the appropriate Schiff base in the presence of hydroxyl or acetate ions or ammonia. The crude products can be recrystallised from an appropriate alcohol or from an aromatic hydrocarbon.

The *o*-hydroxyazobenzene nickel complexes, which can be derived from the corresponding *o*-hydroxyphenolazomethines by replacement of the methine group thereof by a nitrogen atom, are also easily obtainable. The organic components of these complexes have been known for a long time as dyestuffs and are thus large-scale products which can be reacted in a simple manner with nickel hydroxide or nickel salts and ammonia to give the corresponding di- or trichelates and which can be obtained in pure form by crystallisation. In the same way as the *o*-hydroxy- and similarly to the *o*-aminobenzaldimines, the *o*-amino and *o*-pyrrole-azo compounds give poly-chelate divalent nickel complexes. The production thereof does not differ fundamentally from that of the other complexes mentioned.

The divalent cobalt complexes can be produced in an analogous manner but, in this case, it is necessary to work under an atmosphere of inert gas.

The catalysts can be very easily regenerated. Thus, a thermally inactivated catalyst can again be impregnated with a divalent nickel or cobalt complex and subsequently with a small amount of a halogen-containing organo-aluminium compound.

A slight drop in activity occurring after a comparatively long period of working can easily be compensated merely by applying small amounts of halogen-containing organo-aluminium compound to the catalyst.

The heterogeneous catalysts according to the present invention can be used, for example, for the oligomerisation of ethylene, propene, butene, isoprene and butadiene. Furthermore,

65

70

75

80

85

90

95

100

105

110

115

120

125

they can be used for carrying out a co-oligomerisation between mono-olefins and between mono- and diolefins.

Heterogeneous catalysts produced according to the present invention for olefins are simple to produce and are based upon cheap carrier materials. They can be used at ambient temperature and atmospheric pressure and exhibit a high reaction velocity and, in many cases, display a good selectivity. A further advantage of these catalysts is their good activity over long periods of time and the ease with which they can be regenerated.

The oligomerisation or co-oligomerisation of the olefins can be carried out in a solid bed reactor. This can consist, for example, of a vertical glass tube, provided with a cooling jacket, with a length of about 30 cm. and a diameter of about 2 cm. with a fused-in glass sinter plate. The packing level of the catalyst, through which the reactants flow from above, can be 10—15 cm., depending upon the carrier material. The carrier material is preferably used with a particle size of 0.3—0.6 mm. The temperature can be measured by means of displaceable thermo-elements. All working steps up to the impregnation of the catalysts should be carried out under argon, the impregnation process itself preferably being complete at a temperature of about 0°C. in an atmosphere of the olefin which is to be oligomerised.

The following Examples are given for the purpose of illustrating the present invention:

Example 1.

30 g. böhmite are heated to 45°C. within the course of 1 hour, thereafter heated slowly to 110°C. within the course of 6 hours and subsequently maintained at this temperature for 3 hours.

The böhmite thermally pre-treated in this manner is mixed at 50°C., within the course of 3 hours, with a solution of 20 ml. triethyl aluminium sesquichloride in chlorobenzene (1:2). After washing out with chlorobenzene and drying at 40°C., the carrier is impregnated at 0°C. with a solution of 123 mg. bis - (N - n - butyl - salicylideneiminato) nickel in 11 ml. chlorobenzene and subsequently dried at 40°C. Thereafter, the catalyst is treated at 0°C. in an atmosphere of propene, within the course of 1 hour, with 1 ml. triethylaluminium sesquichloride. The propene conversion at 20°C. is 660 v/v.h. Composition of the reaction product:

72% dimers of which 16.5% n-hexenes
20% trimers
8% higher oligomers.

Example 2

30 g. böhmite, which has been pre-treated

in the manner described in Example 1, are mixed with 30 ml. of a solution of triethyl aluminium sesquichloride. After drying the carrier at 70°C., it is impregnated at 0°C. with a solution of 124 mg. bis - (N - n - butyl - salicylideneiminato) nickel in 35 ml. n-hexane. Subsequently, a mixture of propene and argon (1:1) is allowed to flow through at 0°C. The reaction temperature thereby increases to 45°C., in spite of intensive cooling. The propene conversion at 30°C. is 1000 v/v.h. Composition of the reaction product:

70% dimers of which 27% n-hexenes
23.4% trimers
6.6% higher oligomers

The catalyst can be used for several days on end with somewhat reduced effectiveness. If it is stored in an atmosphere of argon, then, even after several weeks, it can still be activated with a small amount of triethyl aluminium sesquichloride to give the initial degree of activity.

Example 3

The böhmite catalyst according to Example 2, inactivated due to an increased reaction temperature, is impregnated with 62 mg. bis - (N - n - butyl - salicylideneiminato) nickel in 50 ml. n-hexane, activated with 0.25 ml. triethyl aluminium sesquichloride and again used for the conversion of propene. The propene conversion at 30°C. is 1000 v/v.h. Composition of the reaction product:

52% dimers of which 10.8% n-hexenes
32% trimers
15% higher oligomers.

Example 4.

30 g. bayerite are continuously heated to 100 a temperature of 95°C. within the course of 4 hours. Thereafter, it is maintained at this temperature for a further 3 hours. The bayerite thermally pre-treated in this manner is mixed with a solution of 40 ml. triethyl aluminium sesquichloride, care being taken that the temperature does not exceed 20°C. In the course of 5 hours, the catalyst bed is dried at a temperature of up to 30°C. After impregnation with a solution of 250 mg. bis - (N - n - butyl - salicylidene - iminato) nickel in 80 ml. n-hexane, the catalyst obtained is used for the conversion of propene. The propene conversion at 50°C. is 2000 v/v.h. Composition of the reaction product:

60—65% dimers of which 20—24% n-hexenes
21—25% trimers
10—19% higher oligomers.

The catalyst has an outstandingly pro-

	63% dimers of which 19% <i>n</i> -hexenes 26% trimers 11% higher oligomers.	60
5	In the case of operating at 65°C., the reaction product had the following composition:	
10	71.5% dimers of which 25.8% <i>n</i> -hexenes 23.0% trimers 5.5% higher oligomers	65
15	The propene conversion is 650 v/v.h.	
20	Example 8	
25	The bayerite catalyst according to Example 4 is used for the oligomerisation of ethylene. The ethylene conversion at 55°C. is 2000 v/v.h. (a).	70
30	After throttling the supply of ethylene to an ethylene conversion of 1500 v/v.h. (b) or to 1000 v/v.h. (c) at 40°C., the reaction products obtained have the following compositions:	75
35	a) 55% butenes 35% hexenes of which 15% <i>n</i> -hexenes 10% higher oligomers, preponderantly octenes	80
40	b) 29% butene 19.8% hexenes of which 28% <i>n</i> -hexenes 31.1% octenes of which 8.7% <i>n</i> -octenes 12.7% decenes 5.8% dodecenes 1.8% tetradecenes	85
45	c) 15.0% butenes 22.9% hexenes of which 28% <i>n</i> -hexenes 28.5% octenes of which 10.5% <i>n</i> -octenes 18.5% decenes of which 4% <i>n</i> -decenes 10.9% dodecenes 4.2% tetradecenes	95
50	Example 9	100
55	Bayerite thermally pre-treated and mixed with triethyl aluminium sesquichloride according to Example 4, is impregnated with a solution of 126 mg. N - (2 - diphenylphosphine - ethyl) - salicylidene - iminato nickel chloride in 100 ml. chlorobenzene and the catalyst so obtained used for the conversion of ethylene. The ethylene conversion at 65°C. is 3000 v/v.h. Composition of the reaction product:	105
	50% butenes 50% hexenes.	110

When the conversion rate is lowered to 1000 v/v.h. by throttling the supply of ethylene and the temperature of the reactor

is maintained at 30°C., then the reaction product obtained has the following composition:

- 5 26% butenes
 38% hexenes of which 10.5% *n*-hexenes
 36% octenes.

Example 10

Bayerite thermally pre-treated and mixed with triethyl aluminium sesquichloride according to Example 4, is impregnated with a solution of 250 mg. bis - (N - *n* - butyl - salicylidene - iminato) cobalt in 35 ml. chlorobenzene and the catalyst obtained is used for the conversion of ethylene.

15 Ethylene conversion at 20°C.: 70 v/v.h.
 ethylene conversion at 50°C.: 120 v/v.h.
 ethylene conversion at 90°C.: 150 v/v.h.

Composition of the reaction product:

100% butenes of which 30—50% but-1-ene.

Example 11

Bayerite thermally pre-treated according to Example 4 is mixed with 50 ml. diethyl aluminium chloride. After removing excess organo-aluminium compound, finally by warming to 30°C. in an atmosphere of argon, the carrier is impregnated at 0°C. in an atmosphere of ethylene, with a solution of 160 mg. bis - (N - *n* - butyl - salicylidene-iminato) cobalt in 20 ml. toluene. Subsequently, the catalyst is dried at 0°C. in an atmosphere of argon, the argon first being passed through a wash bottle containing triethyl aluminium sesquichloride. In the temperature range of 10 to 60°C., the catalyst has an ethylene oligomerisation activity of 170 v/v.h. The reaction product obtained consists exclusively of butenes.

Example 12

40 Bayerite thermally pre-treated and mixed with triethyl aluminium sesquichloride according to Example 4 is impregnated with a solution of 575 mg. bis - (N - *n* - butyl - salicylidene - iminato) cobalt and 41 mg. bis - (N - *n* - butyl - salicylidene - iminato) nickel in 50 ml. chlorobenzene. The ethylene conversion at 10°C. is 200 v/v.h. Composition of the reaction product:

50 9.0% butenes
 20.9% hexenes of which 50% *n*-hexenes
 15.0% octenes of which 8% *n*-octenes
 54.2% decenes of which 3% *n*-decenes
 remainder higher oligomers.

WHAT WE CLAIM IS:—

55 1. Process for the preparation of heterogeneous oligomerisation and co-oligomerisation catalysts for olefins, wherein a completely hydrated aluminium oxide or a

partially dehydrated aluminium hydroxide or a hydroxide group-containing aluminium oxide carrier material is first thermally pre-treated, then reacted with at least one halogen-containing organo-aluminium compound and subsequently impregnated with at least one divalent nickel and/or divalent cobalt complex in which ligand atoms include oxygen, nitrogen, phosphorus arsenic and/or antimony, the reaction and subsequent impregnation being carried out at a temperature of —50 to 150°C.

60

2. Process according to claim 1, wherein one or two coordination positions of the central atom of the divalent nickel and/or divalent cobalt complex is occupied by an amino nitrogen atom.

65

3. Process according to claims 1 or 2, wherein the carrier material is bayerite, hydargillite, böhmite or γ -aluminium oxide.

70

4. Process according to any of the preceding claims, wherein the thermally pre-treated carrier material is reacted with at least one halogen-containing organo-aluminium compound of the general formula

75



in which X is a fluorine, chlorine, bromine or iodine atom and R is an alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, aralkyl or aralkenyl radical.

85

5. Process according to any of the preceding claims, wherein the reaction and subsequent impregnation are carried out at a temperature of 0 to 60°C.

90

6. Process according to any of claims 1 to 4, wherein the reaction with the halogen-containing organo-aluminium compound is carried out at a temperature of —50 to 100°C.

95

7. Process according to claim 6, wherein the reaction with the halogen-containing organo-aluminium compound is carried out at a temperature of about 0°C.

100

8. Process according to any of the preceding claims, wherein, for each 30 ml. of carrier material, there are used 20—50 ml. of halogen-containing organo-aluminium compound.

105

9. Process according to any of the preceding claims, wherein the halogen-containing organo-aluminium compound is used either in undiluted form or dissolved in an inert solvent.

110

10. Process according to any of the preceding claims, wherein the nickel and/or cobalt complex is applied in the form of a solution in an inert solvent.

115

11. Process according to claim 9 or 10, wherein the inert solvent is an aromatic, aliphatic or cycloaliphatic hydrocarbon or a halogenated aliphatic or aromatic hydrocarbon.

120

12. Process according to claim 1 for the

- preparation of heterogeneous oligomerisation and co-oligomerisation catalysts, substantially as hereinbefore described and exemplified.
13. Heterogeneous oligomerisation and co-oligomerisation catalysts, whenever prepared by the process according to any of claims 1 to 11.
14. Process for the regeneration of a catalyst according to claim 13 which has become thermally inactivated, wherein said catalyst is impregnated with at least one divalent nickel and/or cobalt complex as defined in claim 1 or 2 and subsequently impregnated with a small amount of a halogen-containing organo-aluminium compound.
15. Process for the reactivation of a catalyst according to claim 13 which has undergone a small drop in activity, wherein a small amount of at least one halogen-containing organo-aluminium compound is applied to said catalyst.
16. Process for the oligomerisation or co-oligomerisation of at least one mono-olefin and/or at least one diolefin, wherein the reaction is carried out with the use of a catalyst according to claim 13. 25
17. Process of oligomerisation or co-oligomerisation according to claim 16, substantially as hereinbefore described and exemplified. 30
18. Oligomers and co-oligomers, whenever produced by the process according to claim 16 or 17.

VENNER, SHIPLEY & CO.,
Chartered Patent Agents,
Rugby Chambers,
2, Rugby Street,
London, WC1N 3QU.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.